

EFFECTIVE DATE

January 9, 1997

LANL-CST-DP-110, R0

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USE OF ION CHROMATOGRAPHY TO DETERMINE ANION CONCENTRATIONS

LOS ALAMOS QUALITY PROGRAM



APPROVAL FOR RELEASE

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HISTORY OF REVISION

REVISION NO.	EFFECTIVE DATE	PAGES REVISED	REASON FOR CHANGE
R0	01/09/97	N/A	Initial procedure, supersedes LANL-CST-DP-94

Los Alamos

Yucca Mountain Site
Characterization Project

USE OF ION CHROMATOGRAPHY TO DETERMINE ANION CONCENTRATIONS

1.0 PURPOSE

This detailed technical procedure (DP) describes the analytical procedure used to determine anion concentrations in water samples, soil and rock leachates, and other solutions as needed for the Yucca Mountain Site Characterization Project (YMP), using an ion chromatographic system.

2.0 SCOPE

This DP applies to all LANL and LANL-subcontractor YMP personnel who conduct anion analyses using ion chromatography as part of the YMP's Water Movement Test task for Los Alamos National Laboratory (LANL).

3.0 REFERENCES

LANL-CST-DP-92, Sample Leaching to Extract Soluble Chloride and Bromide
LANL-CST-DP-93, Step-Leaching Procedure for Extracting Soluble Chloride and Bromide
LANL-CST-DP-103, Identification, Storage, and Handling of Samples for the Water Movement Test
LANL-YMP-QP-02.7, Personnel Training
LANL-YMP-QP-03.5, Documenting Scientific Investigations
LANL-YMP-QP-12.3, Control of Measuring and Test Equipment and Standards
LANL-YMP-QP-17.6, Records Management
ASTM (1990). D2777-86, Standard Practice for Determination of Precision and Bias of Applicable Methods of Committee D-19 on Water, Vol. 11.01 Water and Environmental Technology, 1990 Annual Book of ASTM Standards.

4.0 DEFINITIONS

4.1 Sample

A sample is a part of a population whose properties are studied to gain information about the whole or group. Examples of samples collected as part of the Water Movement Test include surface and subsurface soils, rocks and fluids, drill cores, cuttings, muck from underground excavations, and biota.

4.2 Leachate

Leachate is the aqueous solution obtained as a result of combining deionized water with a sample of soil or rock and allowing time for readily soluble constituents to dissolve into the water following procedures described in DP-92 and DP-93.

4.3 Chromatogram

A chromatogram is a plot of the response of a detector to the various solutes present in an aqueous sample after the solutes have been analytically separated using a chromatographic method.

4.4 Working Calibration Curve

A working calibration curve represents the relationship between the true concentrations of a specific solute in a suite of standards and the measured peak areas as determined by an analytical detector, under a specific set of operating conditions.

4.5 Precision

Precision refers to the degree of agreement of repeated measurements of the same property. It is expressed quantitatively as the standard deviation of test results about the arithmetic mean and is obtained by repetitive testing of a sample or reference material, such as a standard, under specified conditions.

4.6 Accuracy

Accuracy refers to the degree of agreement between the measured mean value of a property and the true value of that property and is expressed quantitatively as a percent bias of the measurement relative to the true value.

5.0 RESPONSIBILITIES

The following personnel are responsible for the activities identified in section 6.0 of this procedure:

- Principal Investigator (PI) for the Water Movement Test
- YMP personnel performing work to the procedure

6.0 PROCEDURE

The following procedure must be controlled as follows:

- If this procedure cannot be implemented as written, YMP personnel should notify appropriate supervision. If it is determined that a portion of the work cannot be accomplished as described in this DP, or would result in an undesirable situation, that portion of the work will be stopped and not resumed until this procedure is modified or replaced by a new document, or until current work practice is documented in accordance with QP-03.5, subsection 6.1.6.

- Employees may use copies of this procedure printed from the controlled document electronic file; however, employees are responsible for assuring that the correct revision of this procedure is used.
- When this procedure becomes obsolete or superseded, it must be destroyed or marked “superseded” to ensure that this document is not used to perform work.

6.1 Principle

Water samples and soil and rock leachates obtained according to DP-92 and DP-93, or other aqueous solutions (e.g., obtained by digestion of rock samples) are analyzed for anions such as chloride (Cl), bromide (Br) and other anions such as sulfate (SO₄) using an ion chromatography (IC) system or its equivalent (e.g., a high pressure liquid chromatography system, or HPLC). Cl, Br, and SO₄ analyses of these solutions allow for determination of the total masses of these anions in the solutions and the corresponding Br/Cl and Cl/SO₄ ratios, which are useful tracers of fluid flow and rock/water interactions.

In an ion or liquid chromatography system, eluant solution carries the aqueous sample through an anion exchange column where the various anionic species are separated based on their relative affinities for the fixed exchange sites. Anions are detected using a conductivity or other type of detector. Detector response is recorded as peaks in a chromatogram which is generally integrated by the chromatography software program. Anion concentrations in the sample are determined by comparison of sample peak areas with the peak areas in a calibration curve prepared from a suite of standards.

6.2 Equipment and Hardware/Software

Equipment needed to conduct IC analyses is listed below. Not all of the items are absolutely necessary. Items or components equivalent to those listed below (e.g., a uv/vis optical detector instead of a conductivity detector) may be used provided they perform the same function with an acceptable level of performance as judged by the user or the PI.

- ion chromatography system (e.g., Dionex Ion Chromatography System, equipped with a conductivity detector, anion exchange and guard columns, and chemical or electrical suppression system)
- eluant pump (e.g., Dionex Isocratic Pump, Model IP-20)
- autosampler (e.g., Thermo Separations autosampler, Model AS3500) (optional; alternative to manual injection of samples)
- Dionex AI-450 Chromatography Automation Software package, or equivalent
- helium or nitrogen tank and regulator

- water purification system capable of producing deionized water with resistivity greater than 17.5 megohm-cm (calibration not required; see section 6.3.2)
- analytical balance, with minimum of 100 gram capacity and 0.1% sensitivity for quantities greater than 0.4 gram, and 1% sensitivity for quantities less than 0.4 gram (e.g., Mettler Model H54AR)

NOTE: Although anion analyses for this activity will generally use the IC system with the components described above, other configurations, including alternative types of chromatographic systems, are also accepted for use under this DP. If an alternative configuration or chromatographic system is used, an equipment list analogous to that above is included in the logbook in which the data are recorded. The system must also be entered into the M&TE Control System in accordance with requirements of QP-12.3 unless its use qualifies as a one-time-only application, in which case the work must clearly be documented as a prototype or scoping activity in accordance with QP-03.5.

6.2.1 Equipment Malfunctions

Any equipment malfunction occurring during implementation of this procedure is likely to be detectable in the course of conducting work and hence is not expected to have a detrimental effect on the final results. Certain malfunctions of an instrument module will prevent the module from operating, thereby generating no data or stopping operation. Examination of the instrument output relative to expected results may also indicate a malfunction. The water purification system has a meter that indicates the resistivity of the purified water. This meter is checked before each use by the user to verify that the resistivity is within the range of acceptable values, i.e., greater than 17.5 megohm-cm. If a problem arises which can be considered a potential source of error or uncertainty for the results, then it is addressed following section 6.7.

6.2.2 Safety Considerations

Good laboratory and scientific practices are used to protect against injury. In particular, the user should be familiar with securing and handling high-pressure gas cylinders. Applicable LANL and/or LANL-subcontractor safety practices for conducting laboratory work are followed, as appropriate.

6.2.3 Special Handling

Standard solutions are stored in the refrigerator when not in use in order to minimize the potential for evaporative loss.

6.3 Preparatory Verification

6.3.1 Hold Points (N/A)

6.3.2 Calibration

The analytical balance is controlled pursuant to QP-12.3. The chromatography system is calibrated by the user following the procedure described in section 6.5.4 of this DP. The water purification system does not require calibration because the purpose of its meter is limited to altering the user to a failure of the system to produce deionized water, as indicated by the reading on the resistivity meter. Meter failure is indicated by a “zero” reading, at which time the meter is replaced by the vendor.

6.3.3 Environmental Conditions

Work is conducted under normal laboratory conditions of cleanliness, at room temperature.

6.4 Control of Samples

Sample identification and control must be sufficient to trace a sample and its derivatives from its original field location to the point of analysis, and the integrity of the sample must be safeguarded throughout the analytical process. Consequently, users must be trained to DP-103 before they can work with samples analytically, and must follow guidelines set forth in that document for sample control.

6.5 Implementing Procedure

6.5.1 Preparation of Eluant and Standards

6.5.1.1 Preparation of Stock Solutions

The user conducts the following steps, as necessary, to prepare stock solutions of the eluants and standards used in this DP:

- a) If neither stock nor working solutions of eluant and standards are already available, then prepare stock solutions as described in this section, using reagent-grade chemicals, deionized water, a calibrated analytical balance, and Class A volumetric glassware. Other volumetric labware, such as autopipets, may also be used if they can be shown to have adequate accuracy for the task; the results of such a determination must be documented in the lab notebook or logbook.

- b) Prepare a stock eluant solution using NaHCO_3 and Na_2CO_3 . A volume of 1-2 liters is generally a convenient amount with which to work. Molarities must be at least as concentrated as the working solution, and a solution that is about 20 times as concentrated as the working solution works well. For the working solution strength recommended in section 6.5.1.2.a, a convenient strength for the stock eluant would be about 0.034 M NaHCO_3 + 0.036 M Na_2CO_3 .

NOTE: Other eluant solutions may also be used (e.g., a sodium tetraborate solution) provided the relevant information listed in Attachment 1, Item B, is documented.

- c) Prepare a stock solution to be used to prepare working standards using appropriate salts containing the anion of interest (e.g., NaCl , NaBr , and Na_2SO_4). Prior to weighing, oven-dry the salts at a temperature at or above 105°C for at least an hour, then cool them in a desiccator. Standard solutions may contain more than one analyte at the discretion of the user. Record reagent chemical weights to the extent necessary such that the solution strength can be known with an accuracy of 1% or better.

NOTE: Alternatively, commercially-available, certified anion stock solutions can be substituted for the chemist-prepared stock solutions. The preferred stock solutions, if available, are certified standard reference materials obtained from NIST. Documentation of these consumable standards is governed by QP-12.3.

- d) Label the storage container for each stock or primary solution with its concentration, date of preparation, and preparer's initials. The expiration date for the stock standard solutions is six months after preparation, and that for the eluant stock solution is one year. The expiration date for a commercially-available certified stock solution is specified on the certificate of analysis.
- e) Refrigerate each solution in a capped or stoppered bottle or flask when not in use.
- f) In the laboratory notebook or logbook, record the required information listed in Attachment 1, Item B, for this task.

6.5.1.2 Preparation of Working Solutions

The user prepares working solutions as required for use in this DP, as described below:

- a) Prepare the working eluant solution on an as-needed basis by dilution of the stock eluant solution, using volumetric glassware with acceptable accuracy (5% for this solution). An effective concentration for anion analyses using most anion-exchange columns is 1.7 mM NaHCO_3 + 1.8 mM Na_2CO_3 . However, the eluant can be strengthened or weakened to enhance solute separation, at the discretion of the user. Also, other eluant solutions can be used (see note under subsection 6.5.1.1.b).
- b) Prepare working solutions for standards by dilution of the stock solution(s), using Class A volumetric glassware or alternative method capable of providing accuracy of 1% or better. The choice of concentration values and quantities to be prepared is determined by the user, who considers for example whether the purpose is for determination of the working calibration curve (section 6.5.4) or for determination of precision (section 6.5.3).
- c) Label the storage container for each standard solution with its concentration, preparer's initials, preparation date, and expiration date, which is six months after preparation. Label the storage container for the working eluant solution with its concentration and preparer's initials; its expiration date is one week after preparation, but this information need not be put on the label.

NOTE: The above labeling requirements only apply to the primary storage container, and not to autosampler vials containing standard solutions.

- d) Refrigerate these solutions in capped or stoppered bottles or volumetric flasks when not in use.
- e) In the laboratory notebook or logbook, record the required information listed in Attachment 1, Item B, for this task.

6.5.2 Initial Set-Up

The user conducts the tasks listed in this section. Required documentation of the steps in this section is covered in other sections of this DP.

6.5.2.1 Working Solutions

Ensure that working solutions of eluant and standards are brought to room temperature before being used in this DP.

6.5.2.2 Column

Verify that the appropriate analytical column is in the instrument.

NOTE: The unique identifier of the installed column is recorded in steps 6.5.3.3.b (precision data), 6.5.4.3.e (calibration data), and 6.6.1.3 (sample data), as appropriate.

6.5.2.3 Sample Loop

Check the sample loop on the chromatography system prior to beginning analyses in order to ensure that the appropriate size loop is in place. The appropriate sample loop size is one that provides a good peak area response (i.e., narrow, well-defined peak with baseline resolution).

NOTE: The above step is not necessary if the autosampler (section 6.5.5.3) is used for sample injections.

6.5.2.4 Eluant System Preparation

Set up the eluant delivery system, which involves the following generic steps:

- degas the eluant solution,
- turn on the eluant pump,
- pressurize the regenerant reservoir,
- turn on the detector, and
- establish a stable baseline signal on the detector.

6.5.2.5 Detector Settings

Set the OUTPUT range on the detector to the desired level. For a conductivity detector, this level will probably be in the range of 3 μS to 300 μS (i.e., 300 μMho), depending on the anion concentration.

NOTE: This step is programmed into the Methods File of the chromatography automation software package (e.g., Dionex AI-450) if that system is being used.

NOTE: Range settings will be different for other types of detectors; for example, the range setting for an ultraviolet-visible light (uv-vis) optical detector would have units of absorption units (AU) or millivolts.

6.5.3 Determination of Precision

The user determines the precision of results generated by this procedure at least once, and more frequently if judged necessary by the PI, e.g., if a change in analytical conditions or equipment is judged as likely to significantly degrade the precision of the method. Data acquisition and analysis, and the format and content of the summary statements about these data, are described in this section.

6.5.3.1 Number of Replicates

The user calculates the minimum number of replicates by using the following formula:

$$n \geq 1 + \frac{30}{P} \quad \textbf{(Equation 1)}$$

where n represents the number of replicates and P is the number of variables considered, in this case, the number of concentration levels analyzed. For this DP, the number of concentration levels is five or more, and the concentrations must span the range of values expected for the samples.

NOTE: As an example, for 5 levels of concentration, $n=7$. Thus, the user would analyze each standard 7 or more times, resulting in 35 or more data points.

6.5.3.2 Acquisition of Data

The user analyzes the appropriate number of samples following steps 6.5.2 (initial setup), 6.5.5 (sample injection), 6.5.6 (sample analysis), and 6.5.7 (data reprocessing; only if necessary).

NOTE: If the user judges in step 6.5.3.3 below that one or more of the analyses are clearly erroneous, then the data for the suspect analyses are discarded and the user repeats the analysis as necessary to ensure an adequate number of data points per level of concentration.

6.5.3.3 Analysis of Precision Data

The user analyzes the precision data as follows:

- a) Review the chromatograms and evaluate suspected outliers following guidelines in subsections 6.6.1.1 and 6.6.2.
- b) Record required information listed in Attachment 1, item D, for this task.

- c) Calculate the mean peak area and standard deviation for each concentration level.
- d) Calculate a coefficient of variation (CV) for each concentration level by expressing the standard deviation as a percentage of the mean peak area.
- e) Insert in a notebook or logbook an appropriate statement that characterizes the precision of the method, using the following guidelines. Precision, expressed as a coefficient of variation, may be constant within the range examined, or it may vary with concentration in a linear or curvilinear manner. If precision is constant, express it as follows (or with equivalent wording):

“The precision of this procedure, within the range of *<state range of concentrations evaluated>*, is *<CV>%*. The data listed on pages *<state page numbers in this logbook>* were generated using standards prepared from deionized water and may differ from those which would be obtained for actual water samples.”

If precision varies linearly or curvilinearly, present the data in the form of a plot, table or equation expressing the variation of precision as a function of concentration. The accompanying statement reads as follows (or with equivalent wording):

“The precision of this procedure, within the range of *<state range of concentrations evaluated>*, varies with the concentration according to the following *<table, equation or figure, as appropriate>*. The data listed on pages *<state page numbers in this logbook>* were generated using standards prepared from deionized water and may differ from those which would be obtained for actual water samples.”

6.5.4 Analysis of Blanks and Standards

6.5.4.1 Analysis of Blanks

The user:

- a) Ensures that a blank sample, consisting of deionized water, is analyzed each day analyses are conducted.
- b) Runs the blank at the beginning and end of each autosampler carriage (or at the beginning and end of a sample suite, for manually injected samples) in order to

demonstrate that potential interferences from labware and chemicals are negligible and that the analytical system is free of impurities.

6.5.4.2 Analysis of Standards for the Working Calibration Curve

The user:

- a) Determines a working calibration curve at least once a week when samples are being analyzed. The calibration curve must include three or more standards that span the range of concentrations expected for the samples to be analyzed.
- b) Analyzes the appropriate number of standards by following steps 6.5.2 (initial setup), 6.5.5 (sample injection), 6.5.6 (sample analysis), and 6.5.7 (data reprocessing, if necessary). Each standard is measured at least twice.

NOTE: If the user judges in step 6.5.4.3 below that one or more of the analyses are clearly erroneous, then data for the suspect analyses are discarded and the user repeats the analysis as necessary to ensure at least three concentration levels with two acceptable data points per level of concentration.

6.5.4.3 Analysis of Calibration Data

The user reduces and reviews the calibration data as follows:

- a) Review chromatograms and evaluate suspected outliers following guidelines in section 6.6.1.1 and 6.6.2.
- b) Record unique identifiers for each standard solution, standard concentrations, injection numbers and peak areas of retained data. (Required information for QA-traceable data is specified in Attachment 1, Item F.)
- c) If the coefficient of variation (CV) for a given level is less than 10%, then all data from this level are included in the regression data set. Otherwise, if data are excluded from the regression set, the reason for the exclusion is documented.
- d) Obtain a working linear or quadratic calibration curve by regressing measured peak area (x) against true concentration (y) for the analyte of interest, for each retained data point. A linear calibration curve has the form $y = A + Bx$, and a quadratic calibration curve has the form $y = A + Bx + Cx^2$, where A is the y-intercept, and B and C are slope factors. Also calculate the coefficient of determination (r^2) for the regression equation. All of these parameters are

calculated by standard software or by using the regression options within the chromatography automation software package.

- e) Record required information for each calibration curve, as listed in Attachment 1, Item E.
- f) Ascertain the acceptability of the calibration curve. In order to be acceptable for use, a given calibration curve must include at least 3 concentration levels, with $r^2 \geq 0.9900$. If the data do not meet these criteria, discard them, document this in the notebook or logbook, and repeat the calibration process starting from step 6.5.4.2 above.
- g) Ascertain the applicable range of the calibration curve by conducting a bias check. Using the working calibration curve obtained in step 6.5.4.3.d, calculate analyte concentrations from the peak areas of each level of the calibration data set. Document the percent difference (bias) between the calculated and true concentrations for each level in the logbook in which the calibration data are recorded. All levels encompassed by the applicable range of the curve must have a bias that is either less than 10% or less than the CV for this level as determined from the precision data (section 6.5.3.3.e). Define the applicable range of the curve as 80% of the lowest level passing the bias check, up to 120% of the highest level passing the bias check. Document this range in the logbook in which the IC data are recorded.
- h) If warranted by the expected range of sample concentrations, then more than one calibration curve may be calculated from a single calibration data set, with each curve assigned a unique identifier. For example, the level most likely to not pass the bias check is the lowest one. If this occurs, and if any samples are expected to fall within the low end of the curve, then the user returns to step 6.5.4.3.d, recalculates the regression curve, this time excluding the highest one or two levels, and re-evaluates the acceptability of the curve based on the criteria in steps f and g. Then, in the determination of sample concentrations (section 6.6.1.2), the user applies whichever curve is considered most appropriate for the given sample.

6.5.4.4 Calibration Checks

The user ensures that a partial calibration check is conducted, at a minimum, at the end of each autosampler carriage or of the day's run. This check consists of the analysis of a low- to mid-range standard in duplicate.

6.5.5 Sample Injection

The user follows the procedures below in order to document sample sequencing and run conditions (section 6.5.5.1), to inject samples into the ion chromatography system manually (section 6.5.5.2), or to inject samples using an autosampler (section 6.5.5.3).

6.5.5.1 Documentation of Sample Sequence and Run Conditions

Record sample identifiers, injection sequence and injection parameters on a Sample Schedule or Autosampler Carriage Record. Information required for this task for the documentation of QA-traceable data is listed in Attachment 1, Item C.

6.5.5.2 Manual Injection

Manually inject the aqueous sample into the chromatography system, and start data acquisition.

6.5.5.3 Injection using the Autosampler

Load sample vials into the autosampler carriage tray, insert the carriage into the autosampler and close the door, and program injection parameters (injection volume or loop size, number of injections per sample, run time, equilibration delay). Begin injections and data acquisition.

6.5.6 Sample Analysis

After the sample is injected, the computer begins plotting the chromatogram. If a standard is being analyzed, the run can be ended after the last analyte of interest has eluted. However, if a sample is being analyzed, the user waits until any late-eluting species have had time to elute before beginning a new run. Each sample is analyzed at least twice.

6.5.7 Data Reprocessing

After the sample has been analyzed, the user conducts the following steps:

6.5.7.1 Examine the chromatogram to verify that peak identification and baseline resolution were done properly.

6.5.7.2 If appropriate, reprocess the chromatogram data by reintegrating the signal using modified parameters. Data are reprocessed by making the appropriate changes to the Methods File of the chromatography automation software package (e.g.,

Dionex AI-450). Only parameters that affect the integration are included in the reprocessing. There are several reasons that the user might decide to reprocess the data for a sample. If a given peak is not properly identified in the chromatogram, then the solute retention time or component window may need to be changed in the Methods File; and the sample signal is reprocessed with these new values. If the baseline of a peak is not properly resolved, then any of a series of baseline commands can be inserted into the Methods File in order to force baseline resolution; and again the sample signal is reprocessed with these new values. These two examples of reprocessing will produce a quantitatively different peak area.

- 6.5.7.3 If the user judges that the validity of the analytical result for a given sample is unacceptable or otherwise in question, even after reprocessing the raw data, then he may reanalyze the sample by repeating steps 6.5.5 through 6.5.7.

6.5.8 Shut-down Procedure

When analyses have been completed for the day, the user flushes the chromatography system with deionized water (e.g., about 15 minutes at 0.5 mL/min), and then turns off the eluant pump, the detector cell, and the helium or nitrogen gas that pressurizes the regenerant. Such flushing is necessary to remove precipitated salts (e.g., from the buffer solution) from the analytical system in order to protect seals and unions. The helium or nitrogen bubbling through the eluant in the reservoir may be kept on or turned off at the discretion of the user. (If an autosampler is used, follow manufacturer's instructions regarding shutdown of this instrument).

6.6 Data Acquisition and Reduction

6.6.1 Determination of Sample Concentrations

The user reviews and reduces the acquired data as follows:

- 6.6.1.1 The user determines whether the validity of any of the data is in question due to a suspected matrix interference, instrument malfunction, faulty peak integration, or unacceptable changes from the procedure described in this DP. These data should not be included in any subsequent data analysis. They may either be discarded altogether; or, if these data are reported in the logbook, then the reasons for their rejection should be noted in the logbook.

- 6.6.1.2 The user determines anion concentrations in each sample from the measured peak area, by reference to the working calibration curves prepared in sections 6.5.4.2 and 6.5.4.3.
- 6.6.1.3 The user documents conditions under which the sample data were generated, as well as the raw analytical results, and calculates the analyte concentration in the original sample, corrected for any dilution or concentration. These data are recorded in the logbook. Required information to be recorded for QA-traceable samples is listed in Attachment 1, Item F.

6.6.2 Treatment of Statistical Outliers

After analyses have been completed for a given sample or standard, the user reviews the full set of data in order to determine whether any of them can be considered as statistical outliers and thereby discarded from the data base, as follows:

- 6.6.2.1 Calculate the mean analyte concentration and standard deviation for the sample results. If only two analyses are available, record the results of these calculations on a data summary table and go to step 6.6.3. Otherwise, proceed to step 6.6.2.2.
- 6.6.2.2 If three or more analyses have been done for a given sample or standard, with an associated coefficient of variation >10%, then suspected outliers may be identified by comparing their T value to criteria values for the designated significance level. The test criterion for the suspected outlier, x_i , is as follows:

$$T = |x_i - \bar{X}| / SD \quad \textbf{(Equation 2)}$$

where \bar{X} and SD are the current estimates of the mean and standard deviation for all retained peak area data at the concentration of material associated with x_i . A table listing critical values of T at the 5% significance level is provided in Attachment 2. (Application of this test is optional; the PI has the option of excluding outliers from data analysis based on experience.)

- 6.6.2.3 If the T-value exceeds the critical value at the selected significance level, then the outlier may be rejected; enter a note concerning the data rejection in the logbook.
- 6.6.2.4 If any statistical outliers are discarded following the T-test, recalculate the mean and standard deviation from the remaining data points. Record these values in the logbook.

6.6.3 Precision of Measured Data

The user expresses the precision of the final results by the standard deviation calculated for the full set of retained sample results. These results are recorded in the logbook.

6.6.4 Acceptability of Data

Data may be acceptable for use if they meet the following criteria. Conversely, lack of meeting the following criteria may provide the basis for rejecting specific data.

- 6.6.4.1 A blank was analyzed prior to the sample, following guidelines in 6.5.4.1.
- 6.6.4.2 The average peak area of the analyte in the blank analyzed prior to and after the sample was $\leq 5\%$ of that of the sample.
- 6.6.4.3 The calibration curve used to calculate the analyte concentration meets all of the criteria in 6.5.4.2.a, 6.5.4.2.b, and 6.5.4.3.f:
 - it was determined within a week of the sample analyses,
 - the regressed data include 3 or more concentration levels that span the range of sample concentrations, with at least 2 acceptable data points per level, and
 - $r^2 \geq 0.990$.
- 6.6.4.4 The applicable range of the calibration curve has been determined by conducting a bias check following 6.5.4.3.g.
- 6.6.4.5 A partial calibration check was conducted according to guidelines in 6.5.4.4.
- 6.6.4.6 The average analyte concentration of the partial calibration check sample calculated using the working calibration curve was within 10% of the true concentration.
- 6.6.4.7 The sample analyses have been reviewed for outliers (6.6.1.1 and 6.6.2).
- 6.6.4.8 The sample concentrations lie within the applicable range of the working calibration curve (within 20% of either end of the curve).
- 6.6.4.9 Any change from, or modification of, the above requirements has been documented and has been approved by the PI, as

indicated by PI initials and date next to the written discussion of the change.

6.7 Potential Sources of Error and Uncertainty

If a problem arises which can be considered a potential source of error or uncertainty for the results, then the user documents it in the laboratory notebook or logbook. Some of the most common sources of error or uncertainty for ion chromatographic analyses are listed below, with suggested corrective actions which may be taken by the user:

6.7.1 Poor Peak Resolution or Baseline Instability

- 6.7.1.1 Interferences can be caused by substances with retention times that are similar enough to cause overlapping of peak areas. Unresolved peaks may result when the concentration of one of the sample components is more than an order of magnitude greater than that of another component that appears in the chromatogram as an adjacent peak. This problem may be corrected by diluting the sample, changing the eluant or its concentration, or changing the flow rate.
- 6.7.1.2 Water from the sample injection causes a negative peak or dip in the chromatogram when it elutes because its conductivity is less than that of the eluant. Sometimes, the chloride peak begins before the detector has returned to baseline values after this dip. Accurate integration of the chloride peak may require reprocessing the signal with different parameters. Alternatively, reanalysis of the sample with different eluant concentrations or flow rates may provide greater separation between the water dip and the chloride peak, and reanalysis with a different type of eluant, detector, or chromatography system may eliminate the water dip altogether. These latter changes necessitate the derivation of a new calibration curve appropriate to the changed analytical conditions.
- 6.7.1.3 Deterioration in column performance can result from the buildup of contaminants on the exchange resin. Changes in retention times and degraded peak resolution are symptoms of such deterioration.
- 6.7.1.4 Air bubbles in the columns, tubing or detector cell can cause baseline instability and peak variability. The user minimizes the introduction of air into the system during sample injection, and uses degassed eluants.

6.7.2 Contamination

The possibility of sample contamination is reduced by working in a clean environment. Failure to prerinse a filter may give high chloride values.

7.0 RECORDS

Records generated as a result of this DP are entries in laboratory notebooks or logbooks recording analytical conditions and results for samples, standards and blanks. A checklist for laboratory notebook and logbook entries relevant to this DP is provided in Attachment 1. Notebooks and logbooks are records that are controlled by procedure QP-03.5 and are submitted to the Records Processing Center as stand-alone records when closed out, in accordance with QP-17.6.

NOTE: Chromatograms are saved on a computer data file or in a loose-leaf folder until the PI has authorized their disposal. Such disposal is judged warranted on the basis that these data plots merely provide visual verification of the instrument output.

8.0 ACCEPTANCE CRITERIA

The criteria that show the correct implementation of this procedure are the records identified in Section 7.0. The acceptability and precision of the final reported analytical data are evaluated by the PI, taking into account such factors as the criteria listed in Section 6.6.4, the standard deviation of the sample results, the precision of the method as documented per section 6.5.3, the results of the bias checks of the calibration curves, the possible presence of less-than-optimal operating conditions (e.g., matrix interference), and the precision of the balances used as documented pursuant to QP-12.3.

9.0 TRAINING REQUIREMENTS

A prerequisite for this DP is to train to DP-103. Training for this DP requires formal training and is documented pursuant to QP-02.7.

10.0 ATTACHMENTS

Attachment 1: Checklist of Laboratory Notebook and Logbook Entries (3 pages)
Attachment 2: Critical Values for T (Two-Sided Test) for identifying Outliers at a 5% Level of Significance (1 page)

CHECKLIST OF LABORATORY NOTEBOOK AND LOGBOOK ENTRIES

- A. Initial descriptive information. is entered in the laboratory notebook or logbook as appropriate prior to starting a technical procedure and on a continuing basis as experimental and procedural changes dictate. These entries are:
- _____ reference to this DP, including revision number
 - _____ unique identifiers for any calibrated equipment used to conduct work under this DP
 - _____ software identifier for instrument software package, if used
 - _____ other entries required by QP-03.5

NOTE: The above information is to be completed for each of the categories that follow.

- B. Preparation of eluants and standards. Required information includes:
- _____ manufacturer, lot number and chemical formula for chemical reagents used to prepare stock solutions in this DP
 - _____ weight of dry reagents, if used to prepare stock solutions, to level required for 5% precision for eluant preparation
 - _____ weight of dry reagents, if used to prepare stock solutions, to level required for 1% precision for standard preparation
 - _____ volume of deionized water for preparation of stock solutions, with precision of 5% or better for the eluant solution and 1% or better for standards
 - _____ dilutions used to prepare working standard solutions, with precision of 1% or better
 - _____ calculated concentrations or molarities for stock standard and eluant solutions
 - _____ unique identifier assigned to each working standard, showing traceability to the certified reference material from which it was prepared
 - _____ expiration date of stock solutions and working standard solutions (only required on containers)
 - _____ preparer's signature and date
 - _____ other documentation required by QP-12.3 for consumable standards
- C. Identification of samples in an autosampler. (Sample Schedule, or Autosampler Carriage Record). Required information includes:
- _____ unique identifier for loaded carriage (or sample batch for manual injections)
 - _____ loop size/injection volume
 - _____ unique identifier for each sample (assigned per DP-103) and standard being analyzed
 - _____ user's signature and date

D. Determination of precision. Required information includes:

- _____ unique identifier for loaded autosampler carriage (or for sample batch for manual injections)
- _____ unique identifier for each standard used
- _____ unique column identifier
- _____ eluant strength and pump rate
- _____ index or injection number, peak area, and T-value (if necessary) for each retained run
- _____ date of data acquisition
- _____ average peak area, standard deviation, and coefficient of variation, for each concentration level
- _____ statement, table or figure characterizing precision as a function of concentration
- _____ user's signature and date

E. Determination of a working calibration curve. Required information includes:

- _____ unique identifier for loaded autosampler carriage (or sample batch for manual injections)
- _____ unique identifier for each standard solution used
- _____ unique column identifier
- _____ eluant strength and pump rate
- _____ index or injection number and peak area for each retained run
- _____ mean, standard deviation, and coefficient of variation for each concentration level
- _____ type of regression equation (linear, quadratic)
- _____ regression equation parameters (slope factors, y-intercept) for calculation of sample concentration from sample peak area
- _____ r^2 value for regression equation
- _____ unique identifier assigned to each regression equation
- _____ bias check calculations for each level of concentration
- _____ applicable range of calibration curve, based on results of bias check
- _____ user's signature and date

F. Analysis of samples, calibration checks, and blanks. Required information includes:

- _____ unique identifier for loaded autosampler carriage (or sample batch for manual injections)
- _____ date of analyses
- _____ unique column identifier
- _____ eluant strength and pump rate
- _____ unique identifier for each analyzed standard and sample (assigned per DP-103)
- _____ dilution or concentration factor (if any) for sample
- _____ quantity of spike (if any) added to sample
- _____ index or injection number and peak area for each retained run
- _____ calculated solute concentration for samples and calibration checks
- _____ identity of calibration curve used to obtain concentration value
- _____ user's signature and date

G. Preliminary data summary table. Outliers need not be included in this table. Required information for data in the summary table includes:

- _____ unique sample identifier for each sample aliquot
- _____ analysis date or carriage identifier for each result
- _____ index or injection number for each analytical result
- _____ dilution factor
- _____ measured concentration for each analytical result
- _____ concentration corrected for dilution/concentration
- _____ comments on reasons for data in this table that are rejected
- _____ average and standard deviation or % coefficient of variation for retained data
- _____ user's signature and date
- _____ documented results of PI's review of results for acceptability
- _____ PI's signature and date for above review

CRITICAL VALUES FOR T (TWO-SIDED TEST) FOR IDENTIFYING OUTLIERS AT A 5% LEVEL OF SIGNIFICANCE

# of Observations, n	5% Level of Significance	# of Observations, n	5% Level of Significance
3	1.15	20	2.71
4	1.48	21	2.73
5	1.71	22	2.76
6	1.89	23	2.78
7	2.02	24	2.80
8	2.13	25	2.82
9	2.21	30	2.91
10	2.29	35	2.98
11	2.36	40	3.04
12	2.41	45	3.08
13	2.46	50	3.13
14	2.51	60	3.20
15	2.55	70	3.26
16	2.58	80	3.30
17	2.62	90	3.35
18	2.65	100	3.38
19	2.68	---	---

Data source: ASTM (1990). D2777-86, Standard Practice for Determination of Precision and Bias of Applicable Methods of Committee D-19 on Water, Vol. 11.01 Water and Environmental Technology, 1990 Annual Book of ASTM Standards, Table 1 (p. 36) and Table X3.8 (p. 41).